THE CHEMICAL COMPOSITION
of a Garnet from the Crabtree Emerald Mine, Spruce Pine, North Carolina

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A B T R A C T

The chemical composition of members of the garnet group may be determined by measuring the physical properties specific gravity, index of refraction and unit cell edge. A sample of garnet from the pegmatite of the Crabtree Emerald Mine, Spruce Pine, North Carolina, was characterized in this study as having a composition of either:

61.37% Almandine, 24.41% Pyrope, 12.75% Andradite and 1.46% Grossular

or

58.74% Almadine, 25.06% Pyrope, 13.19% Andradite and 3.01% Spessartine

The garnet being investigated occurs in the pegmatite of the Crabtree Emerald Mine, in the Spruce Pine district of Mitchell County, North Carolina. George Kunz (1894) reports this locality as being first discovered in July of 1894 by J. R. Rorison and D. A. Bowman. The tabular pegmatite body varies from 0.6-3 meters in thickness, strikes nearly north-south, dips to the east at approximately 35° and outcrops at several points along the strike for several hundred meters from the mine adit. It is a simple pegmatite, with no apparent zoning, with well defined walls in a country rock of mica schist. The pegmatite is composed chiefly of quartz and albite feldspar (Pratt, 1898), with biotite, black tourmaline, white, yellow and pale-green beryl, emerald, apatite, fluorite, talc and rosy garnet as accessory minerals. The garnet which is under investigation in this study occurs as small crystals 1-4 mm in diameter embedded in a matrix of quartz and feldspar. Generally these crystals are shattered internally and impossible to remove in a single piece. The fragments of these crystals are translucent to transparent and colored a pale reddish-pink with a faint tinge of lavender.

Ford (1915) established that there is a systematic relationship between chemical composition and physical properties of the members of the garnet group. Using 23 selected analyzed garnets with measured specific gravities and indices of refraction very close to the values calculated from their analysis, Ford constructed 8 triangular diagrams with pure end-member garnets at their apices which may be used to relate specific gravity, index of refraction and chemical composition. Each of these triangular diagrams shows the relationship between a different set of three end-member garnets with contour lines showing specific gravity and index of refraction of the three-component compounds.

Knowing the specific gravity and index of refraction of a garnet, the chemical composition of that garnet can be determined by referring to these diagrams. Sriramadas (1957) constructed eight similar triangular diagrams relating chemical composition to the properties of refractive index and unit cell edge, based on the data of Skinner (1956).

The implied assumption in these diagrams is that the physical properties represented on each triangle are additive functions of the molecular proportions of the pure end-member components A,B,C, at the corners; thus the refractive index, n, of a sample would be

$$n = n_A X_A + n_B X_B + n_C X_C$$

throughout the system A-B-C, where n_A , etc., are the indices of the pure end-member components, and X_A , etc., are their respective molecular proportions in the sample. Fleischer (1937) proved that this type of relationship is at least a very good approximation for natural garnets. The main difficulty with these diagrams is that the same set of data may plot on several different diagrams, with no way to establish which is the correct composition. Furthermore, there is no way to show the possibility of four-component or five-component garnets. Winchell (1958) combined the diagrams of Ford and Sriramadas by using index of refraction and unit cell edge as independent variables, the ordinate and abscissa, respectively, and graphing the chemical compositions and specific gravity as functions of these two properties. Index of refraction and unit cell edge are used as the independent variables because both Sriramades (1957) and Winchell (1958) agree that these are the best-measured physical properties. Using Skinner's (1956) values for index of refraction and unit cell edge for the pure end-member components, these end-members are plotted in figures 1 and 2. Each pair of end-members is joined by lines in the conventional manner used to represent the corresponding binary series. These lines outline triangles which correspond to the triangular diagrams of Ford with contour lines on these triangular faces showing the variations of specific gravity. Figure 1 locates the four end-members Pyrope, Almadine, Grossular and Andradite, the four triangles outlined by connecting them, and the contour lines of specific gravity. Figure 2 adds Spessartine and shows the six triangular fields that have spessartine as one apex, with the appropriate specific gravity contour lines. In many cases the contoured specific gravity data resolve ambiguities due to the overlap of the three-component composition fields, and in some cases may permit estimates to be made on the basis of four-component compositions.

The index of refraction n, for the Crabtree Mine garnet was determined by use of the immersion method.

Immersion mounts of crushed garnet and various mixtures of high refractive index fluids were made and studied by the central illumination (Becke Line) method, with a sodium vapor lamp as the light source, until a fluid with a refractive index which matched that of the garnet was found. The refractive index of this fluid was then determined by use of the minimum deviation method. A prism-shaped well was filled with the refraction index fluid and mounted on a single circle goniometer. A beam of light from a sodium vapor lamp was passed through this prism of refractive index fluid and the minimum deviation angle was noted and entered into the following equation to calculate the index of refraction.

$$n = \frac{\sin 1/2\ (M \,\&\, \alpha)}{\sin 1/2\, \alpha}$$

The index of refraction for the garnet was thus determined to be $n = 1.808$

The specific gravity of the garnet was determined by the use of a pycnometer. Table 1 contains the data used to determine the specific gravity. Column 1 gives the weight in grams of the empty pycnometer, column 2, the weight of the pycnometer plus the dry garnet sample, column 3, the weight of the pycnometer, garnet sample, and sufficient water to completely fill the pycnometer, column 4, the weight of pycnometer filled with water. For each line in Table 1 the following calculations were made to determine the specific gravity:

$$\text{(Col. 8) } G = \frac{(2 - 1)}{(2 - 1) - (3 - 4)}$$

Eight determinations of specific gravity were made and the average of these eight determinations results in $G = 4.068$.

The unit cell edge, a_o was determined using both the X-ray powder film method and diffractometer method described below. In the film method several fragments of the garnet were crushed in an agate mortar until very finely powdered. This powder was placed on a clean glass microscope slide, mixed with a drop of collodion and while still wet a glass fiber was pulled through this garnet-collodion mixture to coat it and then allowed to dry. This gives the garnet powder a supporting substrate that is fine enough in diameter to be completely immersed in the tiny beam of X-rays entering the camera, yet stiff enough to not droop while being rotated in that X-ray beam. This garnet coated glass fiber was mounted in a 57.3 mm diameter powder diffraction camera to rotate in a beam of X-rays from an iron anode X-ray tube filtered by manganese foil, giving X-rays with wave length $\lambda = 1.938$ Ångstroms.

After 24 hours of exposure the film was removed from the camera and developed to produce the picture labeled S. P. Garnet.

Data taken from this picture are given in Table 2. Column 1 gives the number of the line, counting from the point where the X-ray beam exited the camera, Column 2 gives the relative intensity of the line being measured, with the darkest line being #10 and the faintest line being #1. Columns 3 and 4 give the readings of the line position in mm, to the left and right of the entrance or exit point of the X-ray beam. Column 5 gives the difference between columns 3 and 4, which in the 57.3 mm diameter camera corresponds to 2 θ. Column 6 gives θ. Column 7 is d, cell dimension, obtained by entering θ from column 6 into the equation

$$d = {}^{1}/_{2}\ (\lambda \text{cosec}\ \ \theta).$$

Column 8 is the hkl of the crystal lattis layer which reflected the X-rays to form the line on the film. Entering the figures from columns 7 and 8 into the equation

$$a_o = d \,/\!\sqrt{h^2+k^2+l^2}_{L}$$

gives column 9, a_o, unit cell edge in Ångstroms.

To get the correct value of a_o that the values of a_o for each line indicate is best, the θ for each line was entered into the equation

$$X = ({}^{1}/_{2}\left(\frac{cos^2\theta}{\sin\theta} + \frac{cos^2\theta}{\theta}\right)$$

X is column 10 and each value of a_o was plotted on a graph of X versus a_o in fig. 3. The point at which the line that best fit the plotted data intersected X = 0, at a_o = 11.579, was taken as being the corrected value of a_o.

A second determination of unit cell edge, a_o, was made using the strip chart X-ray diffractometer. A slurry of finely powdered garnet mixed with alcohol was spread on a glass sample holder and allowed to dry. A strip chart was made of this sample between the 2 θ values of 30° and 134° using unfiltered beam of X-rays from an iron anode X-ray tube. The resulting chart appears as figure #4. Data taken from this chart appear in Table #3. Column 1 gives the position of the peak in °2 θ, column 2 gives interplanar spacing, d, column 3 gives the corresponding value of $h^2+k^2+l^2$, and column 4 gives the value of the unit cell edge, a_o, in Ångstroms. Taking the average of the last 5 values of a_o, we arrived at the corrected value of a_o = 11.579 Å.

Plotting the measured values for index of refraction and unit cell edge of the garnet being investigated on Figure 1 or 2 the point plots into three of the three-component triangular area, Al-Py-An,Al-Gr-Py and Al-Sp-Py. The three compositions and specific gravities indicated are

59.9% Al	26.2% Py	13.9% An	G=4.0614
77.75% Al	17.75% Gr	4.5% Py	G=4.1567
58.45% Sp	37.45% Al	4.1% Py	G=4.2143

Comparing the measured specific gravity with the calculated specific gravities shows that none of these three-component compositions is the proper composition but rather a combination is necessary to give the proper percentage of each of two of the three-component garnets which are in the sample. To determine the percentage of each three-component garnet which is needed, the following equation is used

#10 $G_{(a)}\,P + G_{(b)}\,(1-P) = G$ measured

Where $G_{(a)}$ and $G_{(b)}$ are the specific gravities indicated from the three-component triangles, G measured is the measured specific gravity of the sample, and P is the percentage of the three-component garnet with specific gravity $G_{(a)}$. From this the proper four-component garnet with the measured specific gravity may be calculated by the following equation

$$P(A_a + B_a + C_a) + (1-P)\ (B_b + C_b + D_b) = (A + B + C + D)$$

where $(A_a + B_a + C_a)$ and $(B_b + C_b + D_b)$ are the molecular proportions of the pure components A,B,C,D in the three-component garnets with specific gravities $G_{(a)}$ and $G_{(b)}$ respectively, P is the percentage of the three-component garnet with the specific gravity $G_{(a)}$, and (A + B + C + D) is the composition of the four-component garnet with the measured specific gravity.

Of the three-component garnets indicated Al – Gr – Py and Sp – Al – Py both have specific gravities that are higher than the measured value, and therefore there is no four-component garnet between them which will have the proper G. Using 4.0614 as $G_{(a)}$ and 4.1567 as $G_{(b)}$ and 4.068 as G(measured) in equation #10 gives P = .9175 and the composition of the four-component garnet between (Al-Py-An) and (Al-Gr-Py) may be estimated as 61.37% Al, 24.41% Py, 12.75% An, 1.46% Gr. Alternatively, we find by similar reasoning the four-component garnet between (Al-Py-An) and (Sp-Al-Py) to have the composition 58.74% Al, 25.06% Py, 13.19% An, 3.01% Sp: in fact, there is a five-component series between these two four-component compositions in every part of which the calculated a_o, n, and G would be the same.

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A P P E N D I X

Table 1

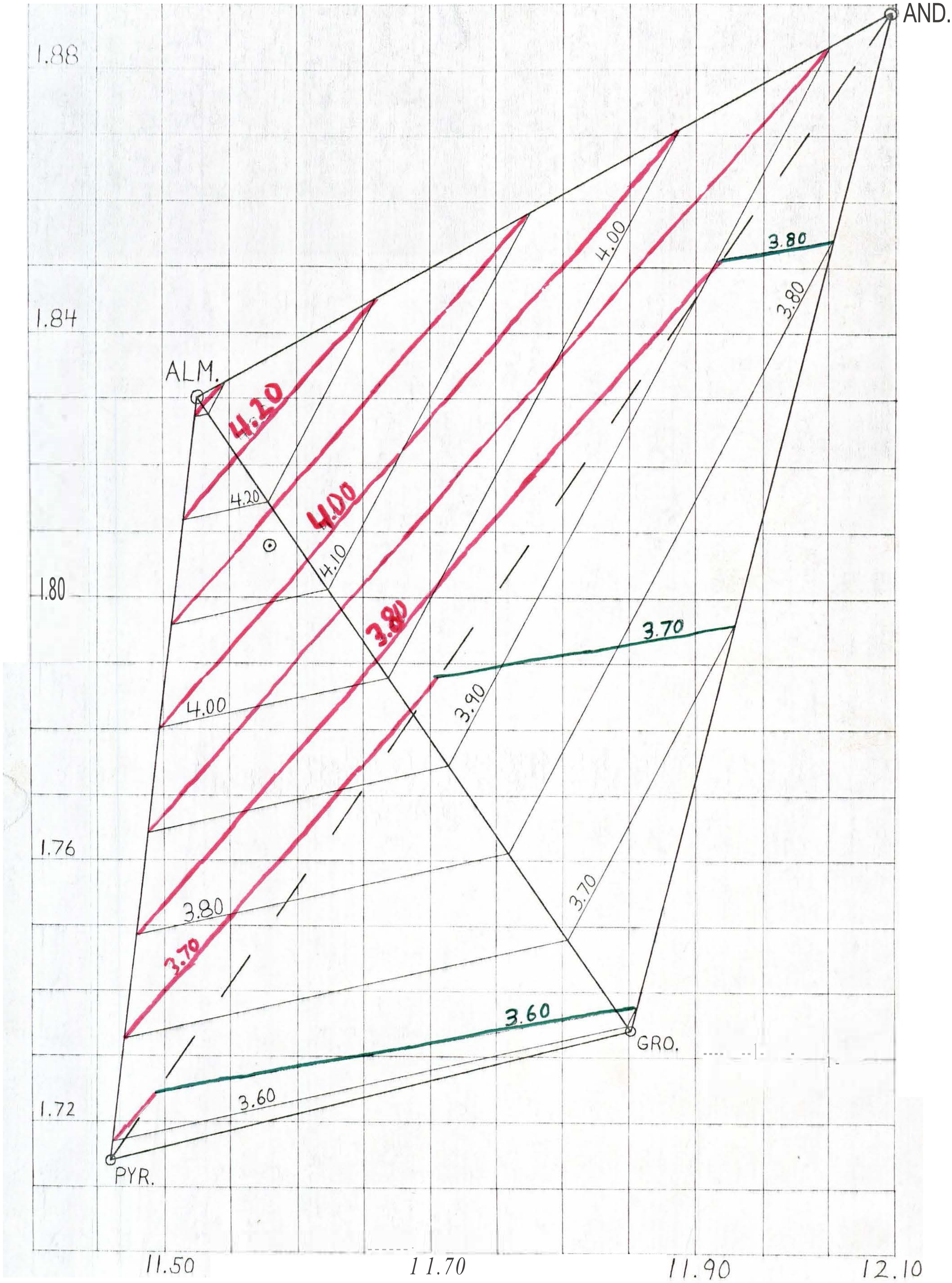
1	2	3	4	5
8.6206	9.3581	12.0405	11.4841	4.0723
8.6206	9.3565	12.0418	11.4861	4.0821
8.6203	9.3551	12.0403	11.4860	4.0709
8.6203	9.3533	12.0359	11.4841	4.0452
8.6204	9.3350	12.0232	11.4842	4.0695
8.6206	9.3371	12.0277	11.4870	4.0756
8.6206	9.3348	12.0216	11.4833	4.0603

Table 2

1	2	3	4	5	6	7	8	9	10
1		308.80	275.10	33.70	16.85	3.3417	222		3.148
2		311.45	272.35	39.10	19.55	2.8947	400	11.5788	2.636
3	10	313.85	269.85	44.00	22.00	2.5858	420	11.5640	2.267
4	2	315.00	268.80	46.20	23.10	2.4689	332	11.5802	2.128
5	4	316.10	267.60	48.50	24.25	2.3584	422	11.5538	2.000
6	4	317.15	266.55	50.60	25.30	2.2666	510	11.5574	1.882
7	4	319.20	264.50	54.70	27.35	2.1084	521	11.5482	1.690
8	1	320.15	263.75	56.40	28.20	2.0498	440	11.5954	1.611
9	5	323.00	260.80	62.20	31.10	1.8753	611	11.5601	1.385
10	4	327.35	256.45	70.90	35.45	1.6701	444	11.5708	1.111
11	6	329.10	254.70	74.40	37.20	1.6021	640	11.5529	1.013
12	7	330.75	253.00	77.75	38.88	1.5433	642	11.5490	.933
13	3	333.90	249.85	84.05	42.02	1.4406	800	11.5248	.789
14	4	243.40	160.30	83.10	48.45	1.2943	840	11.5766	.556
15	5	241.70	161.70	80.00	50.00	1.2645	842	11.5893	.506
16	4	240.15	163.35	76.80	51.60	1.2360	664	11.5947	.460
17	1	239.35	164.30	75.05	52.48	1.2214	930	11.5872	.436
18	3	236.05	167.60	68.45	55.78	1.1715	941	11.5972	.353
19	2	233.40	170.20	63.20	58.40	1.1373	10.2.0	11.5982	.296
20	1	230.55	172.95	57.60	61.20	1.1054	10.3.1	11.5935	.241
21	7	227.65	175.95	51.70	64.15	1.0763	10.4.0	11.5921	.190
22	6	225.50	178.10	47.40	66.30	1.0577	10.4.2	11.5865	.158
23	6	220.75	182.85	37.90	71.05	1.0241	880	11.5864	.098

Table 3

1	2	3	4
33.60	3.3513	12	11.6092
39.10	2.8947	16	11.5788
43.90	2.5913	20	11.5886
46.20	2.4689	22	11.5802
48.40	2.3630	24	11.5763
50.60	2.2666	26	11.5574
54.70	2.1084	30	11.5482
56.60	2.0432	32	11.5581
62.20	1.8753	38	11.5601
69.20	1.7058	46	11.5693
70.90	1.6701	48	11.5708
74.40	1.6021	52	11.5529
77.50	1.5475	56	11.5804
84.00	1.4476	64	11.5808
96.90	1.2943	80	11.5766
100.20	1.2626	84	11.5719
111.80	1.1698	98	11.5804
128.60	1.0750	116	11.5781
132.60	1.0579	120	11.5887


AND.
1.88
1.84
ALM.
4.20
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1.80
3.80
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1.76
3.70
3.80
3.70
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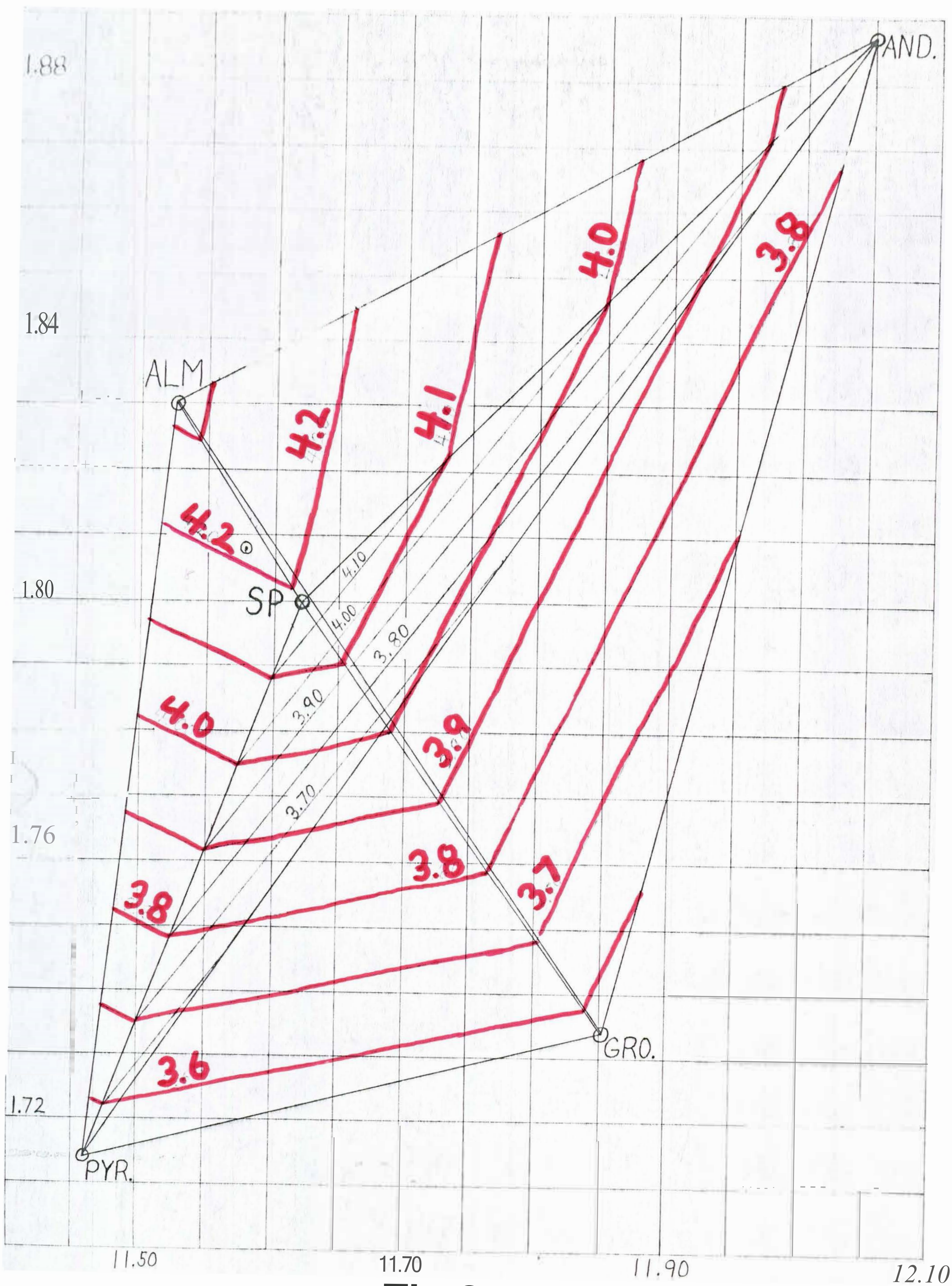
GRO.
1.72
3.60
PYR.
11.50
11.70
11.90
12.10

Fig.1



1.88
1.84
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Fig.2

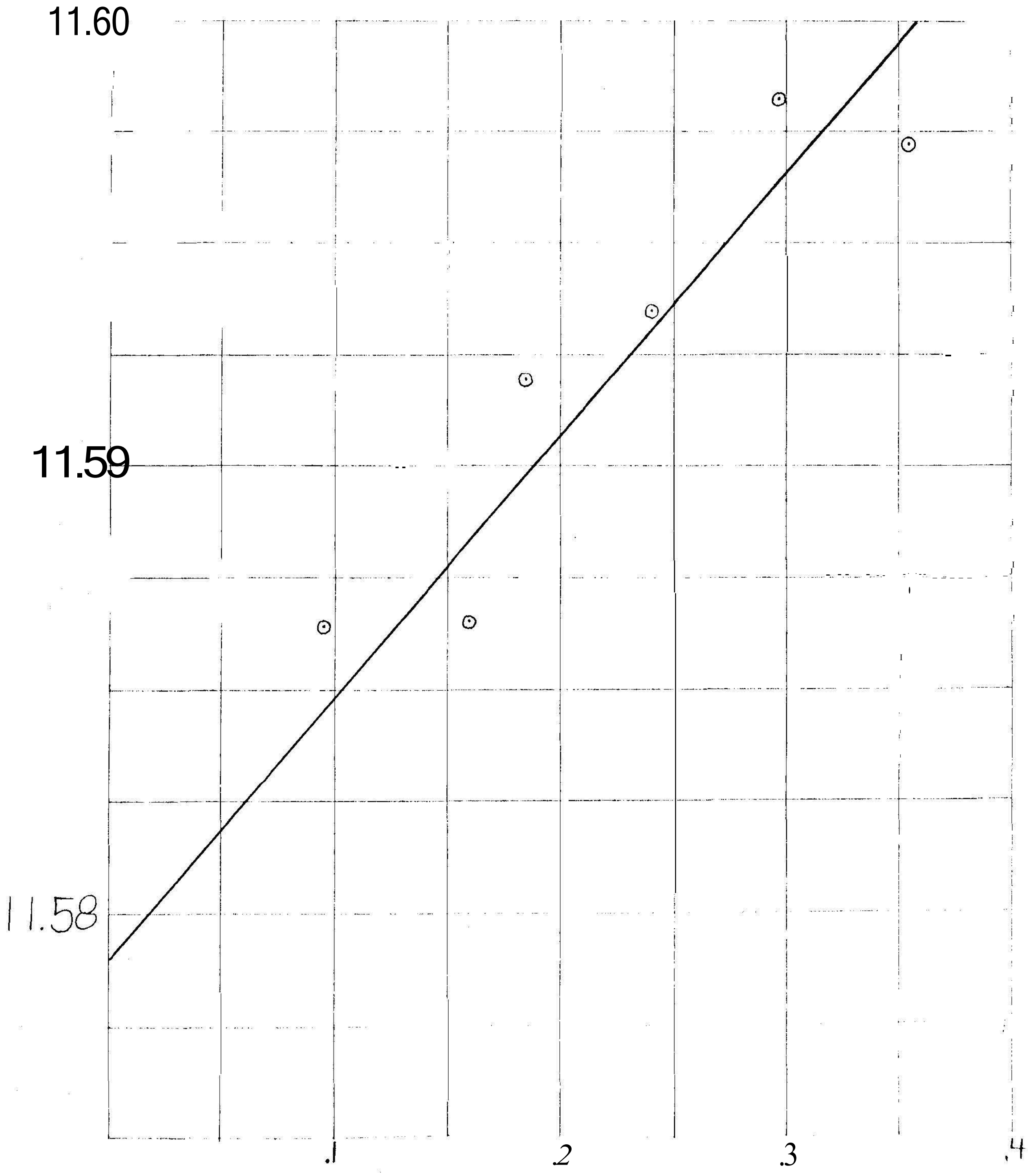


Fig. 3

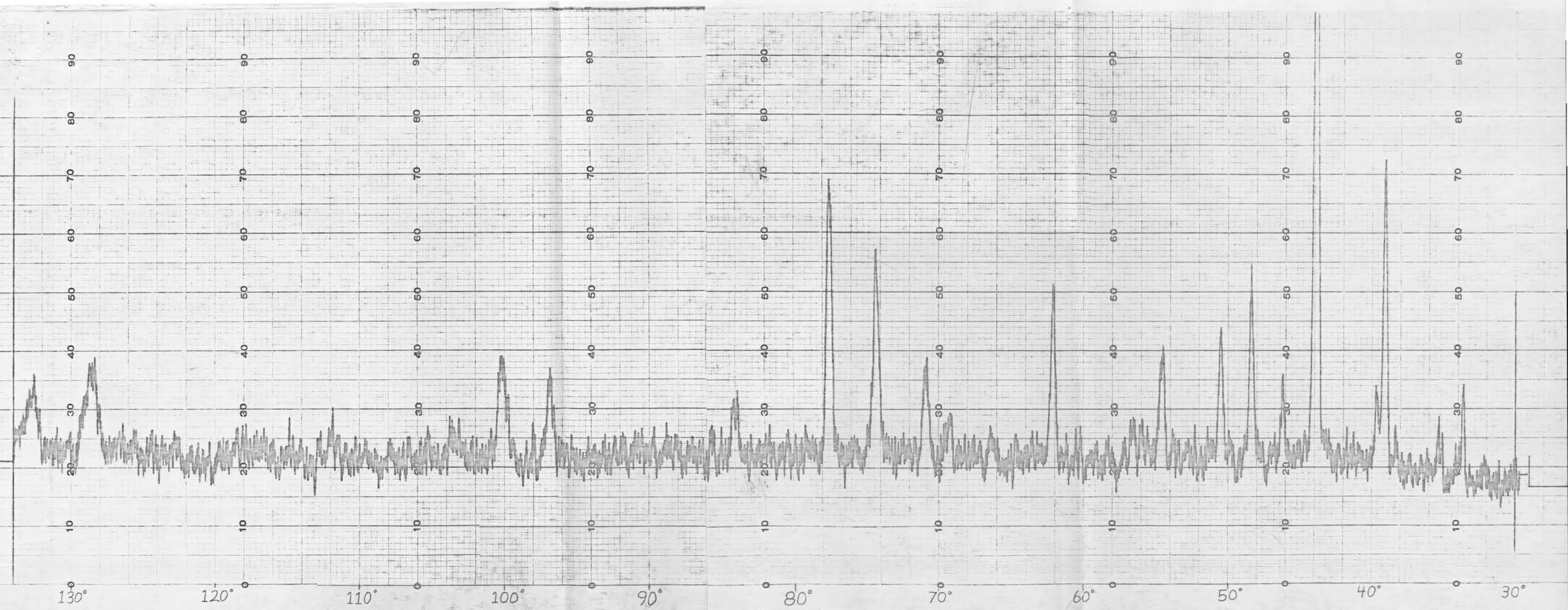
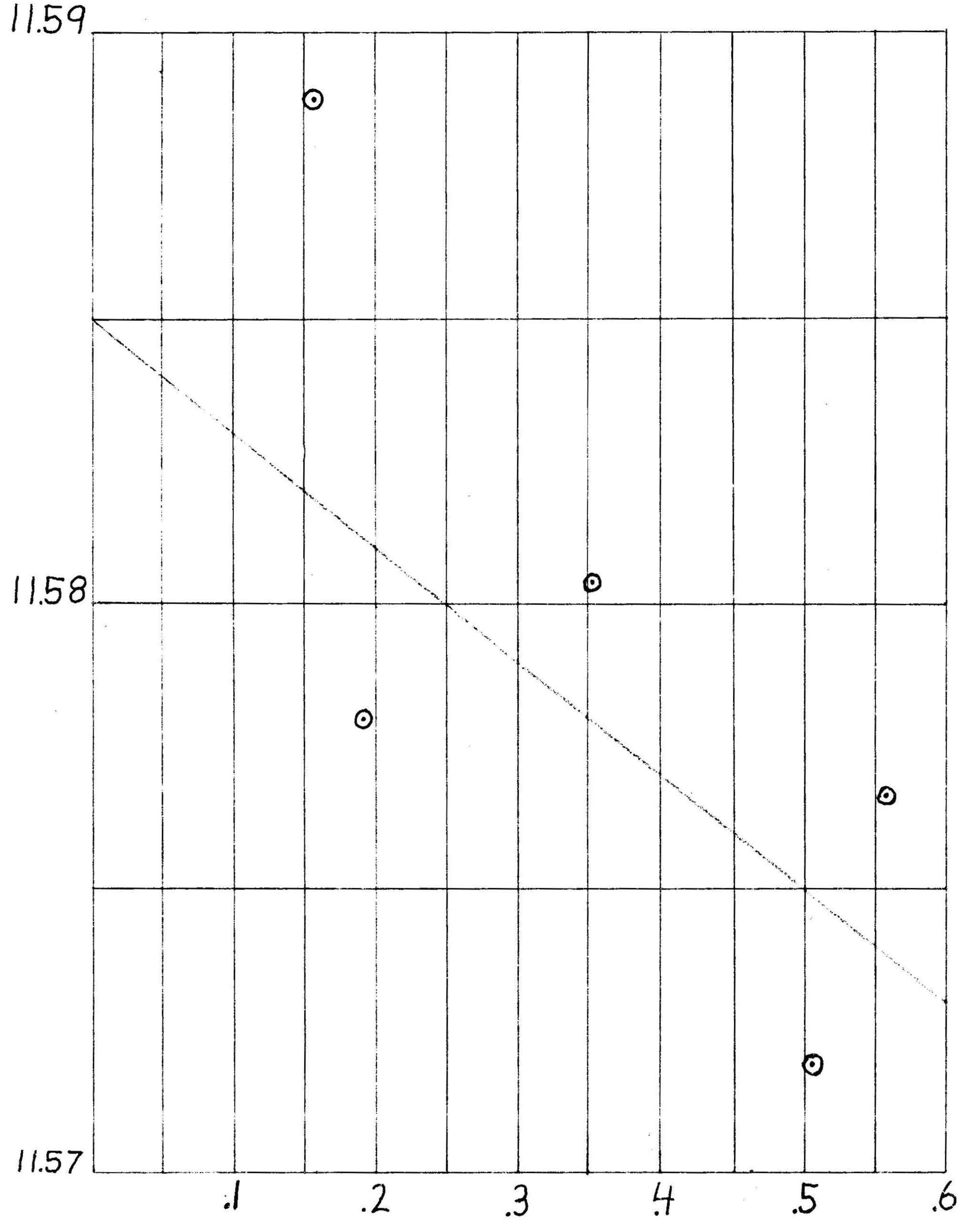


Fig. 4

Fig. 5



SP Garnet